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CHEMISTRY OF PLUTONIUM (V)

1. Potential of the Plutonium (V)/(VI) Couple
Ionic Species of Plutonium(V) in Acidic Solutions

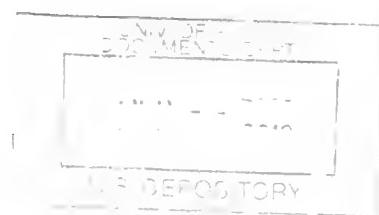
by

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1. Potential of the Plutonium(V)/(VI) Couple Ionic Species of Plutonium(V) in Acidic Solutions

By K. A. Kraus and G. E. Moore

ABSTRACT

Through potentiometric titrations, the potential of the Pu(V)/(VI) couple in chloride and perchlorate solutions was found to be ca. -0.93 v near pH 3 at 25°C. Since this value is in reasonably good agreement with a potential previously determined for an 0.5M HCl solution, and since the hydrolytic behavior of Pu(VI) is sufficiently well known, it can be concluded that the Pu(V) species in acidic solutions is PuO_2^{+} with an undetermined number of water molecules of hydration. This conclusion was confirmed through pH measurements during reduction of Pu(VI) to Pu(V) near pH 3.

1. INTRODUCTION

As it became apparent that Pu(V) is reasonably stable in solutions of low acidity (even in the presence of excess of certain reducing agents) and that Pu(V) solutions can be prepared instantaneously by reduction with a number of reagents, including iodide ions, it appeared feasible to determine the potential of the Pu(V)/(VI) couple through direct emf measurements. The potential of this couple had previously been estimated from disproportionation data by Connick, McVey, and Sheline¹ for an 0.5M HCl solution, and thus a measurement at considerably lower acidity (e.g., pH 3) coupled with a knowledge of the hydrolytic behavior of Pu(VI) would permit identification of the species of Pu(V) which exists in these solutions.

2. EXPERIMENTAL

The potential of the Pu(V)/(VI) couple in chloride and perchlorate solutions was determined through potentiometric titrations of Pu(VI) solutions using iodide ions as reducing agents. This method was chosen rather than the potential determination of a series of solutions for which the ratio of Pu(V) to Pu(VI) is known, since (a) the concentration of Pu(V) cannot be estimated with precision spectrophotometrically because of the low extinction coefficient of its most prominent peak, and since (b) by the use of this method an independent check could be obtained on the "reversibility" of the couple.

The titration of a Pu(VI) chloride solution was carried out in the standard manner near 25°C using a saturated KCl-calomel electrode as a reference, and using saturated KCl as the liquid junction. In order to minimize possible interference through complexing of Pu(V) or Pu(VI) by chloride ions, a very dilute chloride solution was chosen for the experiment.

Several titrations of perchlorate solutions were carried out. Since the results agreed reasonably well, only the last of these will be described here. The titration was carried out in a special vessel, which for temperature control of both the solution and the saturated KCl-calomel reference electrode was partially immersed in a thermostat whose temperature was $25.0 \pm 0.1^\circ\text{C}$.

The titration vessel was conical in shape (maximum capacity 10 ml; 3 to 5 ml of solution were used in the experiment), contained a side-arm for the insertion of a microburette, a small platinum wire (used as the redox electrode) sealed into the wall of the vessel, and a cap constructed of a standard tapered female ground glass joint, through which a small air stirrer could be inserted. Contact with a salt bridge was made using an asbestos wick through the bottom of the titration vessel. To avoid precipitation of potassium perchlorate, the bridge was divided by two microstopcocks to permit the use of three different electrolytes in series—1.45M NaClO₄, 2.68M NaNO₃, and saturated KCl, the latter being in a ca. 25 cc conical vessel into which a standard (Beckman) calomel electrode was placed. It was found necessary to permit thermal equilibration of the calomel cell for several days to obtain reproducible readings.

Both before and after the titration of the perchlorate solution, the calomel electrode was calibrated against a quinhydrone electrode. For this purpose quinhydrone was dissolved in 0.09921M HCl. Assuming the standard quinhydrone half-cell potential to be -0.6990 volts^{2,3} and assuming the activity coefficient of oxonium ions to be 0.841 for 0.1M HCl,⁴ the calomel half-cell potential was found to be -0.2543 ± 0.0003 volts. The difference of this value from that usually assumed (-0.246 volts)⁵ is probably due to the inclusion of the arithmetical sum of the various liquid junction potentials of the system.

The potential measurements were carried out with a Beckman Model G pH meter (chloride solution) and a Leeds and Northrup Type K potentiometer (perchlorate solution). Some difficulties were encountered in finding stable potential readings after the addition of each new aliquot of sodium iodide solution. The potentials drifted for many minutes, and to get the "final" reading it was necessary either to wait ca. one-half hour to one hour to get constancy, i.e., drift less than 0.01 mv/minute, or to extrapolate a series of readings. Probably only a small part of this drift was due to poor stirring of the solution. Instead, the drift suggests that either the Pu(V)/(VI) couple is reversible only to a limited extent, or, more probably, that the measuring electrode did not behave perfectly. From the reasonably good agreement of the experimental points with a line of theoretical slope (see Section 3) it can be concluded, however, that the drift in the readings did not seriously affect the final results. In this connection it is interesting that a similar difficulty was later observed in the determination of the potential of the Np(V)/(VI) couple.⁶

Analysis for the various oxidation states of plutonium was carried out spectrophotometrically with a Beckman quartz Model DU spectrophotometer. Using the extinction coefficients given in another paper,⁷ the calculations were carried out according to the "3-point ratio" method previously described.⁸ The plutonium concentrations were determined through standard radiochemical alpha assay.

The Pu(VI) solutions were prepared from Pu(VI) nitrate solutions through two "barium (poly)plutonate" cycles,⁹ consisting of precipitation with excess barium hydroxide and dissolution in a small amount of the requisite acid. The composition of the solutions before titration was

- a) Chloride solution: 6.25×10^{-4} M Pu, pH 3.18, 0.002M Cl⁻, $\mu^* = 0.01$
- b) Perchlorate solution: 1.65×10^{-2} M Pu, pH 3.14, 0.039M ClO₄⁻, $\mu = 0.11$.

When the iodide titration was ca. 50% complete, the ionic strength of the Pu(VI) perchlorate solution was increased to 1.0 through addition of concentrated sodium perchlorate, to determine the difference in the potentials at the two ionic strengths.

Solutions (a) and (b) contained 96% and 67% Pu(VI) and ca. 3% and ca. 26% Pu(V), respectively, as determined through a combination of the iodimetric and spectrophotometric data. (The end-point of the potentiometric titration could be identified with reasonably high precision since a large potential change occurs there. This suggests that an iodimetric titration of Pu(VI) to Pu(V) near pH 3 could be used in the quantitative analysis of plutonium. The method appears to be limited only by the purity of the original Pu(VI) solution with respect to other oxidation states of plutonium, since as shown in

* μ represents ionic strength.

separate experiments, the presence of excess iodide ions does not cause reduction to Pu(IV) or Pu(III) near that pH.) Solution (b) also contained several per cent polymeric Pu(IV).

Using a glass electrode and a Beckman Model G pH meter, the pH of the solutions was measured before and after the titration.

3. RESULTS AND DISCUSSION

The results of the potential measurements have been summarized in Figures 1 and 2, where the observed potentials have been plotted against $\log \frac{(\text{Pu(VI)})^*}{(\text{Pu(V)})}$ (determined from the iodometric data).

A line of slope -0.0591 was drawn through the experimental points, since they should fall along such a line according to the equation

$$E = E^\circ - 0.0591 \log \frac{(\text{Pu(VI)})}{(\text{Pu(V)})} - 0.0591 \log \frac{\alpha_{\text{Pu(VI)}}}{\alpha_{\text{Pu(V)}}} + \epsilon \quad (1)$$

where E = observed cell potential

E° = standard cell potential (without liquid junction)

α = activity coefficient (subscript denotes species)

ϵ = sum of liquid junction potentials

Parentheses indicate concentrations in moles/liter.

The agreement and thus the precision of the measurements appear to be satisfactory, especially for the perchlorate solution (Figure 2), where sufficient time was taken to obtain equilibrium readings, indicating that the drifts in potential reading did not seriously interfere.

The cell potentials for unit ratios of Pu(VI) to Pu(V) were 0.687 volts (chloride solutions), 0.6808 volts (perchlorate solution, $\mu = 0.11$), and 0.6848 volts (perchlorate solution, $\mu = 1.0$). From these the formal half-cell potential of the Pu(V)/(VI) couple for the chloride solution can readily be evaluated by assuming zero liquid junction potential (at the saturated KCl bridge), and -0.246 volts for the standard potential of the calomel half-cell.⁸ The value thus obtained for the Pu(V)/(VI) potential is -0.933 volts.[†] The uncertainty of this value has been arbitrarily set at ± 0.005 volts, since the calomel electrode was not separately calibrated and differences of this order of magnitude can be expected. The assumption that the liquid junction potential was zero is probably reasonably good.¹⁰

Evaluation of the formal potential for the Pu(V)/(VI) couple in perchlorate solution is considerably more difficult because of the uncertainty connected with the estimation of the various liquid junction potentials of the system. Of these, the liquid junction potentials at the junction 1.45M NaClO₄ - 0.0992M HCl (saturated with quinhydrone) is both the most difficult to evaluate and probably also the largest. The assumption that the sum of the liquid junction potentials and the potential of the calomel half-cell is -0.2543 ± 0.0003 volts is applicable only for the standardization measurement, since the liquid junction potential would be different during the measurements on the plutonium-perchlorate solution. Since this change of the liquid junction potentials cannot be readily evaluated, it will be assumed that it remains constant, although this will then introduce a large uncertainty (arbitrarily set at ± 0.015 volts) for the value of the Pu(V)/(VI) potential in perchlorate solution. Using -0.254 volts as the reference potential, the value -0.935 volts for the potential of the Pu(V)/(VI) couple at ionic strength $\mu = 0.11$ can be calculated.

* Parentheses indicate concentration in moles/liter.

† "Formal" potentials refer to unit ratios of the concentrations of the oxidized and reduced species, rather than unit activities of all species, as is the case with "standard" potentials.

‡ For the reaction Pu(V) \rightarrow Pu(VI) + E⁻.

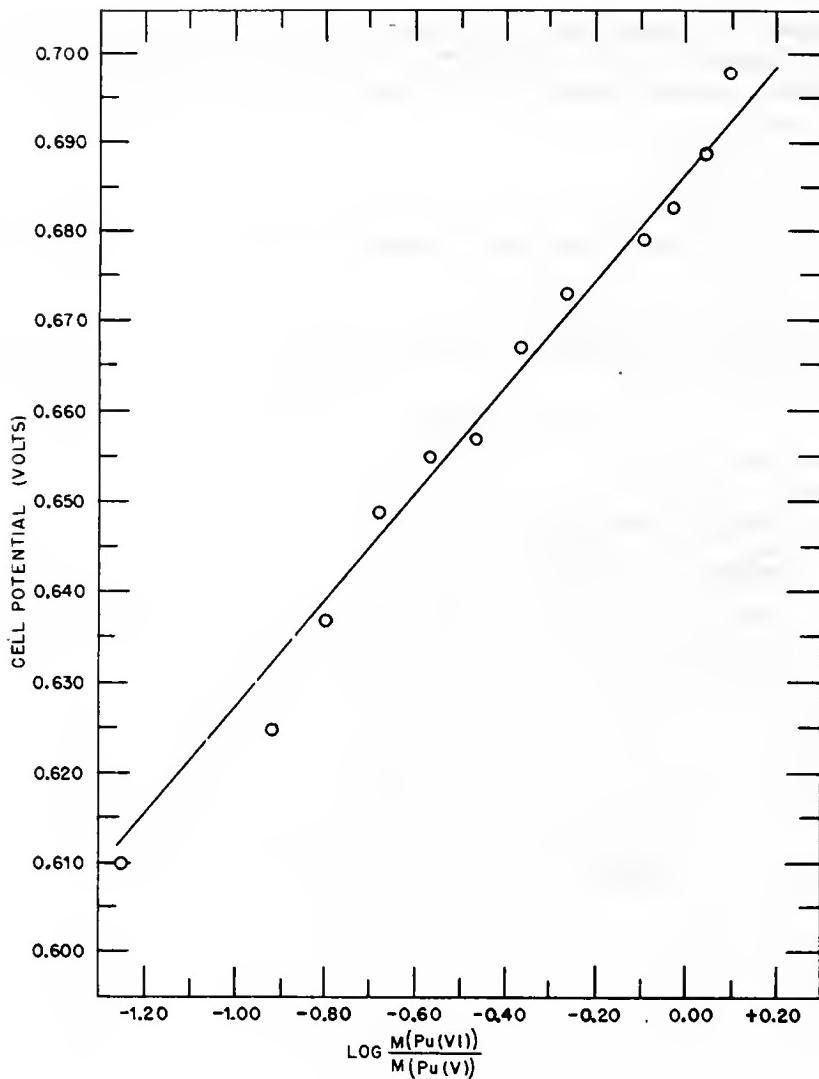


Figure 1. Observed cell potentials for chloride solutions.

- Observed potential
- Solid line has theoretical slope of 0.0591 volts

The half-cell potential at ionic strength $\mu = 1$ appears to be practically the same since the small difference in the observed cell potentials lies within the expected change of the liquid junction potentials, and thus no further significance can be attached to it.

The agreement of the potentials in the chloride and perchlorate solutions is surprising in view of the uncertainties connected with the measurements of each potential. The data show, however, that it is entirely unlikely that under the conditions of the experiment chloride ions complex Pu(V). This is in agreement with later experiments.⁷ (At the time these experiments were carried out, chloride complexing of Pu(V) could not entirely be excluded, even for the highly dilute chloride solutions used,

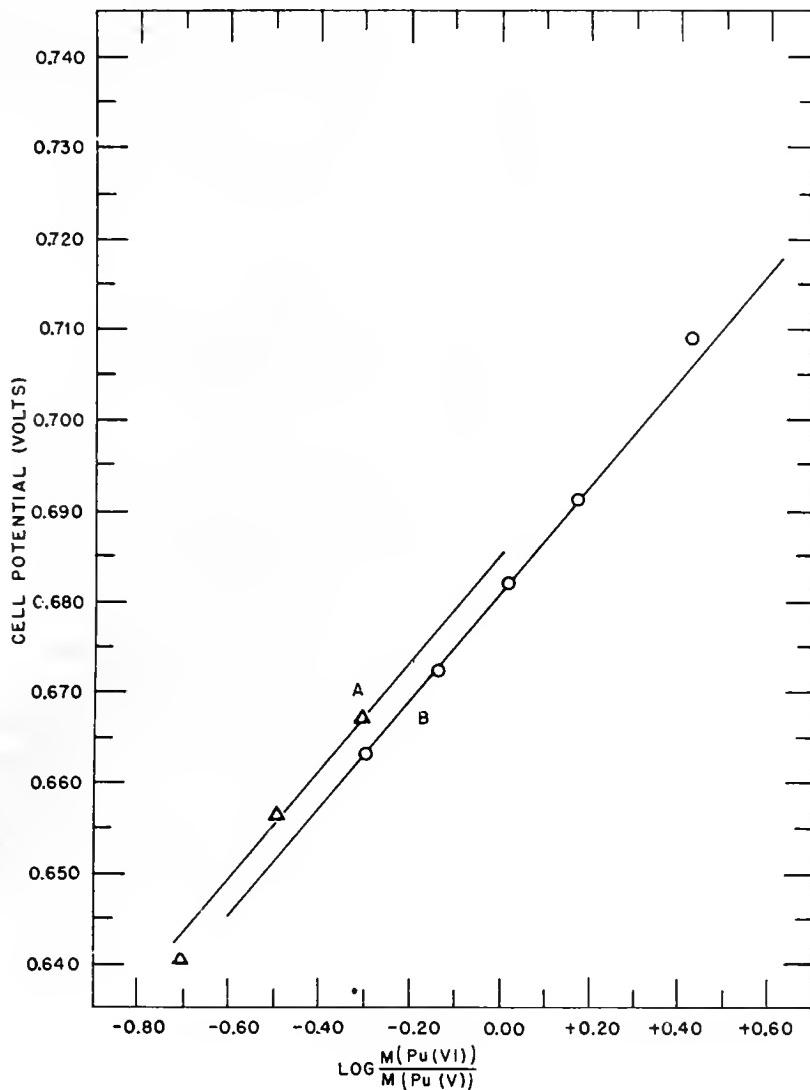


Figure 2. Observed cell potentials for perchlorate solutions.

- Observed potentials $\mu = 0.11$
- △ Observed potentials $\mu = 1.0$.
- Lines A and B have theoretical slope of 0.0591 volts

since very little was known regarding the chemical properties of Pu(V). From our present knowledge of its chemistry, however, it appears very unlikely that complexing of Pu(V) would take place even in concentrated chloride solutions. More experiments are necessary to prove this point conclusively. Chloride complexing of Pu(VI) would be expected to occur only at very much higher concentrations of chloride ions.¹¹⁾

Comparison of the potential data determined near pH 3 with those determined at higher acidity (0.5M HCl) is of interest since from this comparison identification of the Pu(V) species in acidic solutions is possible. The value reported by Connick et al.¹ for 0.5M HCl is -0.912 volts.* Some complexing of Pu(VI) by chloride ions is known to occur in 0.5M HCl¹¹ and therefore a somewhat more negative potential would be predicted for the uncomplexed species. Since the stability content of the chloride-Pu(VI) complex is unknown, the difference in the potentials can only be estimated, and probably amounts to ca. 10 to 20 mv. This would make the Pu(V)/(VI) potential in 0.5M HCl, after correction for chloride complexing, ca. -0.92 to -0.93 volts—in reasonably good agreement with the value determined here at pH ca. 3—showing that the potential of the couple is practically pH independent in this range of acidities.

It is generally assumed that Pu(VI) in acidic solutions is PuO_2^{++} ,¹³ and it was shown that primarily the same species is still present near pH 3.¹⁴ Since the constancy of the potential shows that hydroxide ions are neither liberated nor used up in the reduction of Pu(VI) to Pu(V), one can conclude that Pu(V) in these solutions is symbolically represented by PuO_2^+ with an undetermined number of water molecules of hydration. This conclusion is in accord with that based on disproportionation studies.¹¹

The conclusion that the formula PuO_2^+ represents the ionic species of Pu(V) in acidic solutions is also confirmed by the results of the pH measurements before and after reduction, from which the number of hydroxide ions (or oxonium ions) liberated in the reaction $\text{Pu(VI)} + \text{I}^- \rightarrow \text{Pu(V)} + 1/2 \text{I}_2$ can be deduced. Since Pu(VI) near pH 3 is primarily PuO_2^{++} , and since hydroxide ions are neither liberated nor used up in the oxidation of I^- to I_2 , all pH changes reflect the difference in the number of hydroxide ions (or oxide ions) of PuO_2^{++} and the Pu(V) species in the solutions.

The pH of the chloride solution changed from 3.18 to 3.25 during the titration. Since this pH change is very small compared with that expected on liberation of one hydroxide ion per Pu(VI) ion reduced, it can be concluded that the number of hydroxide ions on Pu(V) and Pu(VI) is the same, i.e., that for Pu(V) the formula is PuO_2^+ . The slight increase in pH cannot be due to dilution of the solution, but probably is due to the fact that the Pu(VI) solution previously had been at a high pH and that because of the hysteresis effect of Pu(VI) a small amount of this species was still hydrolyzed.¹³ The pH of the perchlorate solution changed from 3.14 to 3.31. The bulk of this change can be accounted for by dilution resulting from the addition of the concentrated sodium perchlorate solution during the experiment. The rest of the change is probably primarily due to the change in ionic strength of the solution and the resulting change of the activity coefficients of the oxonium ions. From both of these experiments, therefore, as well as from a number of similar experiments, the conclusion just reached, that the ionic species of Pu(V) in acidic solution is PuO_2^+ , is well substantiated.

*This potential was originally given as -0.92 volts by Connick, McVey and Shcline, and was apparently re-evaluated by Connick,¹² whose value is used here.

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